InP AND GaAs SURFACE CHARACTERIZATION WITH VARIABLE STOICHIOMETRY OBTAINED BY MOLECULAR SPRAY

APPLICATIONS TO THE MANUFACTURE OF SCHOTTKY DIODES

J. Massies, N.T. Linh, J. Olivier, P. Faulconnier and R. Poirier

Translation of "Etude de surfaces de phosphure d'indium obtenues sous differentes stoichiometries par la technique des jets moleculaires. Application a la realisation de barrieres de Schottky", Laboratoire Central de Recherches Thomson-CSF, Orsay (France), Final Report, LCR-2270-DK, August 1977, 31 pages

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16. Abstract   Both InP and GaAs surfaces were studied in parallel. A molecular spray technique was used to obtain two semiconductor surfaces with different superficial compositions. The structures of these surfaces were examined by electron diffraction. Electron energy loss was measured spectroscopically in order to determine surface electrical characteristics. The results are used to support conclusions relative to the role of surface composition in establishing a Schottky barrier effect in semiconductor devices.

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25 May 1978

Dear Mr. Poirier:

In August, 1977, you published a research report entitled: InP
AND GaAs SURFACE CHARACTERIZATION WITH VARIABLE STOICHIOMETRY OBTAINED
BY MOLECULAR SPRAY. APPLICATIONS TO THE MANUFACTURE OF SCHOTTKY DIODES.

With the approval of Mr. Nicolas, we propose to transmit this
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executed with that organization. For this purpose, we would be grate-
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Furthermore, Mr. Nicolas has also approved the publication of
an abstract of this report under the heading "Laboratory Activities"
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the text.

Thank you very much.

[signature]
J. Sevin

Summary

Clean GaAs (001) and InP (001) surfaces were obtained through ion milling under an ultra-vacuum. Utilizing the molecular spray epitaxy technique and by means of arsenic or phosphorus adsorption, these surfaces were created with different compositions which are more or less rich in arsenic or phosphorus. Thus, these surfaces have characteristic structures which differ from those of the bulk material. Low-energy electron diffraction reveals up to eight different superstructures.

The electronic surface state caused by broken bonds was studied through low-energy electron spectroscopy. It was concluded that there is an absence of energy level surface states located within the semiconductor forbidden band. Consequently, the existence of a Schottky barrier in a metal/GaAs or metal/InP contact cannot be attributed to intrinsic semiconductor surface states.

In situ metallization experiments on surfaces with different compositions (clean or oxidized) caused Schottky contacts whose barriers are more or less high. This variation in the barrier can be attributed to two effects: chemical (contamination by impurities) and structural (arrangement of atoms at the interface).

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1. Introduction   /1*

In 1947, Bardeen [1] proposed a model for the metal/semiconductor interface in which the height of the Schottky barrier is independent of the metal and is wholly determined by the doping and by the surface properties of the semiconductor. More specifically, these properties are the surface states located at the semiconductor gap, and which determine the Fermi level at the metal/semiconductor interface. Much later, Mead and Spitzer [2] analyzed the experimental results for a large number of IV and III-V semiconductors in interaction with various metals, and demonstrated that the determination of the Fermi level at the metal/semiconductor interface varies very little with the work function of the metal, in accordance with the preceding model.

When we proposed the present study, photoemission research had just allowed Eastman and Freeouf [3] to make a satisfactory correlation of the locations of surface states for the free surfaces of several III-V semiconductors with the Schottky barrier values published by Mead and Spitzer. Since these surface states were due to broken bonds in gallium atoms, it appeared to us to be worthwhile to study the influence of surface composition on the existence of such states, on the one hand, and on the Schottky barrier value, on the other hand. We have shown (in a previous study, DRME No. 74 34 296) that in the case of III-V semiconductors, it is possible to control the surface composition by utilizing the molecular spray technique [4].

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*Numbers in the margin indicate pagination in the foreign text.

Thus, the purpose of this study is:

-- to obtain InP (100) surfaces with differing stoichiometries
by means of molecular sprays, and to characterize them by
low-energy electron diffraction and Auger spectrometry;

-- to study the chemical reactivity of these surfaces with re-
spect to oxygen, and

-- to realize in situ metallizations on these surfaces and to
determine the possible effect of their stoichiometry on the
properties of the metal/semiconductor interface.

Initially, therefore, the research was projected for InP, but
upon the request of the DGRST, we have included the study of GaAs.
However, in spite of the effort to preserve the goals of the study,
we found it necessary to minimize the research on reactivity with
oxygen (inasmuch as this subject had been recently researched by the
IBM Esaki team [5]). On the other hand, the results we obtained for
GaAs are ample.

2. Study and Operations Format

Research was carried out with the collaboration of the Monocrys-
talline Substances Laboratory and the Interface Physics Laboratory,
according to the following plan:

the Monocrystalline Substances Laboratory was responsible for:
-- obtaining clean surfaces with various compositions utilizing
the molecular spray technique
-- characterization of these surfaces
-- studying the electronic properties of these surfaces through
low-energy electron spectroscopy
-- determining surface states with respect to broken gallium
bonds
-- creating Schottky barriers by in situ metallization
-- electrical characterizations of the Schottky barriers

the Interface Physics Laboratory was responsible for:
-- [determining the] effect of oxygen on InP
-- Auger profile characterization of the Au-InP interface

3. Results

3.1 Obtaining Clean Surfaces with Differing Stoichiometries

3.1.1 Gallium Arsenide

The conditions for obtaining clean GaAs (001) surfaces with variations in stoichiometry yielding compositions with surfaces rich in arsenic or rich in gallium were established through utilization of molecular sprays during the preceding DRME study (see Figure 1 for equipment utilized).

Upon completion of that study, we were first able, in fact, to detect, by means of low-energy electron diffraction (LEED), the orthogonal supersturctures c(8x2) and c(2x8). The corresponding arsenic recovery rate θ_{As} for these two superstructures is 0 and 0.5, respectively. Other superstructures such as (1x6) and (3x1) were also noted and were considered to be characteristic of transient phases. We shall utilize the notation: GaAs (001) Ga c(8x2) in order to specify the orientation of the crystal, the gallium-rich characteristic, and the superstructure obtained.

In this study, we have more specifically explored the region in which θ_{As} is more than 0.5. This range can be observed only when the temperature of the substrate is less than 450°C. Therefore, we found ourselves to be concerned with arsenic adsorption conditions: arsenic spray incident to the surface at isotropic pressure of 5×10^{-7} Torr (essentially As_2). Thus, we were able to determine two principal structures corresponding to arsenic adsorption at the surface: GaAs (001) As (1x1) ($\theta_{As} \sim 1$) and GaAs (001) As c(4x4) ($0.5 < \theta_{As} < 1$).

A c(6x4) superstructure was also observed, but under insufficiently defined conditions, which prevented reproducibility.

These results are summarized in Table 1. An example of LEED patterns is shown in Figure 2.
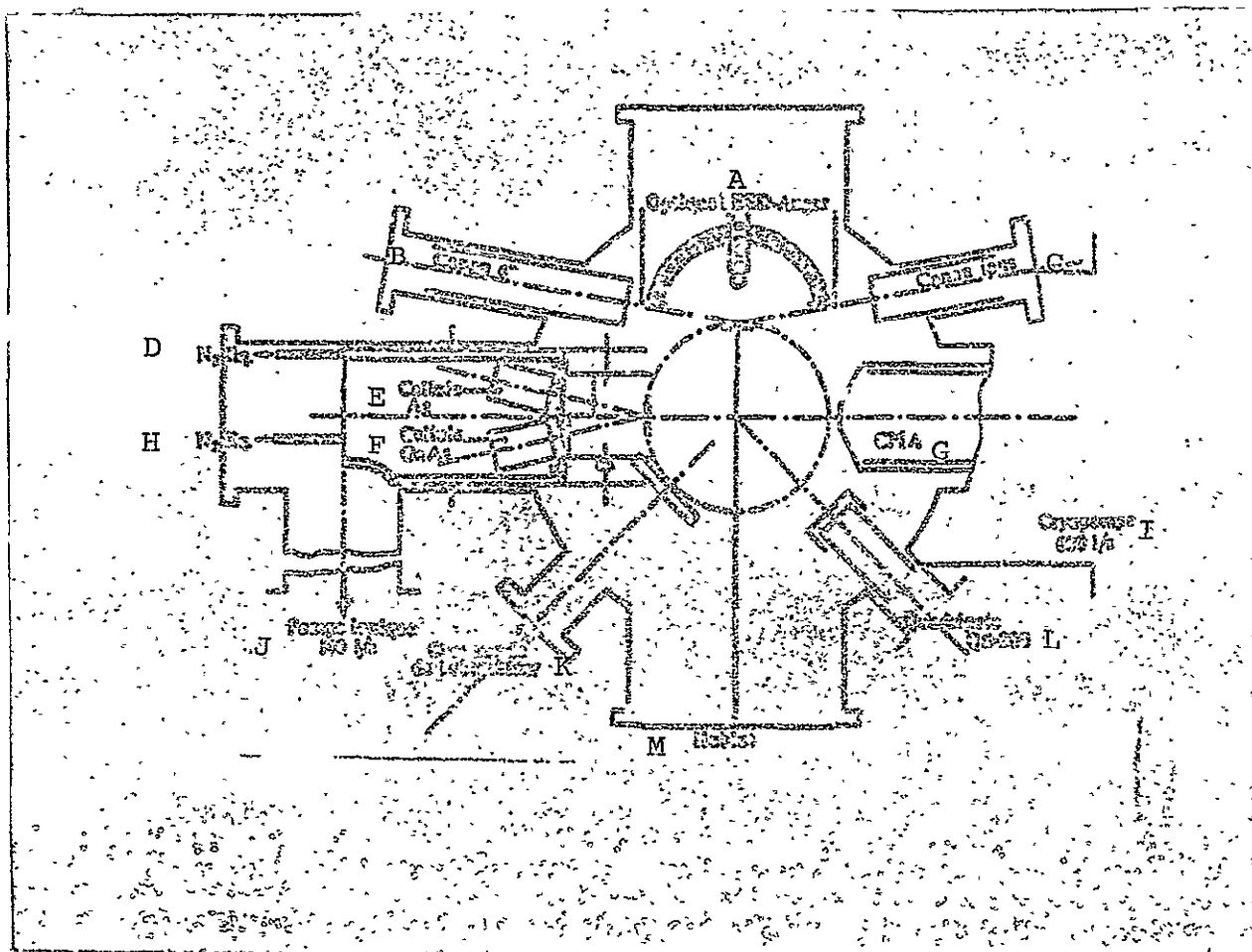
Figure 1. Apparatus in which the following operations occur
conjointly: epitaxy by means of molecular sprays,
surface analysis and metallization of contacts.

KEY: A. Auger/LEED optics   H. [illegible]
      B. e⁻ gun   I. Cryogenic pump
      C. Ion gun   J. Ion pump
      D. [illegible]   K. [illegible]
      E. Ag cell   L. [illegible]
      F. GaAs cell   M. [illegible]
      G. CMA

A

B

Figure 2. Examples of low-energy electron diffraction patterns.
A. GaAs (001) As c(2x8)
B. GaAs (001) As c(4x4)

TABLE 1

EFFECT OF SURFACE STOICHIOMETRY ON THE STRUCTURE OF GaAs (001)

temperature	650	550	(500 - 450)	(350-200)	150
structures A	c(8x2) (4x1) (3x1) (2x3) c(2x8)			c(4x4)	(1x1)
d'obtention B	épitaxie ou recuit de c(2x8) C			adsorption O As ou recuit de (2x1) D	
taux de recouvrement θ_As E	∼ 0		∼ 0.5		∼ 1

KEY: A. Superstructures   D. (1x1) As adsorption or
      B. Means by which   annealing
          obtained   E. Recovery rate θ_{As}
      C. x(2x8) epitaxy or
          annealing

3.1.2 Indium Phosphide

A. InP (001) In

As it does for GaAs, Auger spectroscopy reveals that the (001) plane of indium phosphide, prepared by means by mechano-chemical polishing (Br_2/CH_3OH), is contaminated by carbon and by oxygen. Therefore, it is necessary, as in the gase of gallium arsenide, to proceed with controlled ion milling.

One half-hour of bombardment with argon ions at 200 to 200 eV is generally sufficient to remove the carbon and most of the oxygen. Correspondingly, the phosphorus peak at 120 eV is considerably more intense. While annealing for several minutes at 300°C may be sufficient to entirely eliminate the oxygen, it does not allow a good LEED pattern to be obtained for the surface in question. At 350°C, the pattern is still very diffuse and perturbed by a slight facetting, but a (4x1) superstructure is apparent. Beyond this temperature, the surface is the seat of a preferential evaporation of phosphorus (in fact, the P^+ and P^{++} species are detected by a quadrupolar mass spectrometer located opposite the sample). Nevertheless, it is necessary to raise the annealing temperature to 450 - 500°C in order to obtain a good quality LEED pattern. In this temperature range, a diffuse median line appears where one can observe diffraction spots in accordance with a (4x2) surface superstructure. Upon observation of the phosphorus loss, this surface is deemed to be stabilized indium ($\theta_P \sim 0$) and will be referred to as InP (001) In (4x2). /7

B. InP (001) P

As in the case og GaAs, we sought to obtain, by means of the molecular spray technique, surfaces with differing stoichiometries from those obtained by simple annealing. Within the scope of this study, an effusion cell identical to that utilized in the case of GaAs, but filled with indium phosphide, was utilized. (Such a source may yield phosphide and indium fluxes in proportions which vary greatly with the temperature.) In spite of the exploration of a wide range of sam-

ple temperatures and phosphorus pressures, no new superstructures were discerned, except one (1x1) obtained by phosphorus saturation, analogous to the (1x1) which we observed for GaAs. The phosphorus enrichment of this surface is also verified by Auger spectrometry. Suspecting that the phosphorus was responsible for this very different behavior of the (001) surfaces of the GaAs and InP, we were led to study the interaction of an arsenic flux on an InP surface.

C. InP (001) As

If InP (001) In (4x2) is subjected to annealing at approximately 500°C under an arsenic flux (isotopic pressure of 5×10^{-7} Torr), a rotation of 90° of the LEED pattern can be observed, which thus becomes 2x4 with a very diffuse line at badly resolved spots. (Therefore, strictly speaking, there is here some uncertainty between the descriptive terms "2x4" and "c(2x8)."

The fact that these experimental conditions for this structural change ($500°C/5 \times 10^{-7}$ Torr As_2) are the same as those in the case of GaAs (001) causes the c(8x2) ($\theta_{As} \sim 0$) pattern to become a c(2x8) ($\theta_{As} \sim 0.5$) pattern, illustrates the analogousness of the interaction of arsenic with the GaAs (001) Ga c(8x2) and InP (001) In (4x2) surfaces. Nevertheless, this analogy cannot be extended to its conclusion. Thus, all the tests performed in order to obtain superstructures analogous to those of c(4x4) ($0.5 < \theta_{As} < 1$) and 1x1 ($\theta_{As} \sim 1$) have, so far, been unsuccessful.

In conclusion, the behavior of an InP (001) surface with respect to stoichiometry and to the superstructures is slightly different from that of GaAs (001). The extreme volatility of phosphorus and its great oxidizability may be the causes. Therefore, a reservation must be made with respect to the similarity which, to a certain extent, one might expect between the surface and interface properties of these two III-V semiconductors.

3.2 Electrostimulated InP Oxidation

Under pressure within the apparatus on the order of 10^{-9} Torr, it has been observed that in the impact area of the electronic analysis beam, there is oxygen fixation and oxidation of the surface of the InP being studied. If one begins with a clean surface whose Auger spectrum is the same as that shown in Figure 3c, one arrives in due time at a spectrum of the type shown in Figure 3b. (The spectrum shown in Figure 3a corresponds to a surface which has been oxidized in ambient air. The presence of carbon, chlorine and sulfur can be observed.)

Figure 4 illustrates the Auger peaks of low- and high-energy phosphorus at two different points of the InP surface: one extremely oxidized, and the other only slightly oxidized. The Auger electrons with energy E = 120 eV (L_3VV) and those with energy E = 1860 eV (KL_2L_2) have mean free paths on the order of 5 angstroms and 20 angstroms, respectively.

The decrease in amplitude of the high-energy peaks allows us to dismiss the explanation of the disappearance under oxidation of the low-energy Auger peak for phosphorus by crossed P-O transitions.

It can be concluded that phosphorus is released from the first monolayers of the InP. This release is undoubtedly due to the cumulative effect of the following phenomena:

-- first, the fixation of oxygen atoms which penetrate the substrate and bond themselves to the phosphorus under the effect of electronic bombardment so as to form an extremely volatile oxide. An analogous result [6] was found when InP surfaces were exposed to increasing oxygen pressures.

-- Second, the localized heating at the point of impact of the /9 beam can reach temperatures on the order of 300°C and above, at which temperatures the desorption of P_2 and P_4 has been observed [7].

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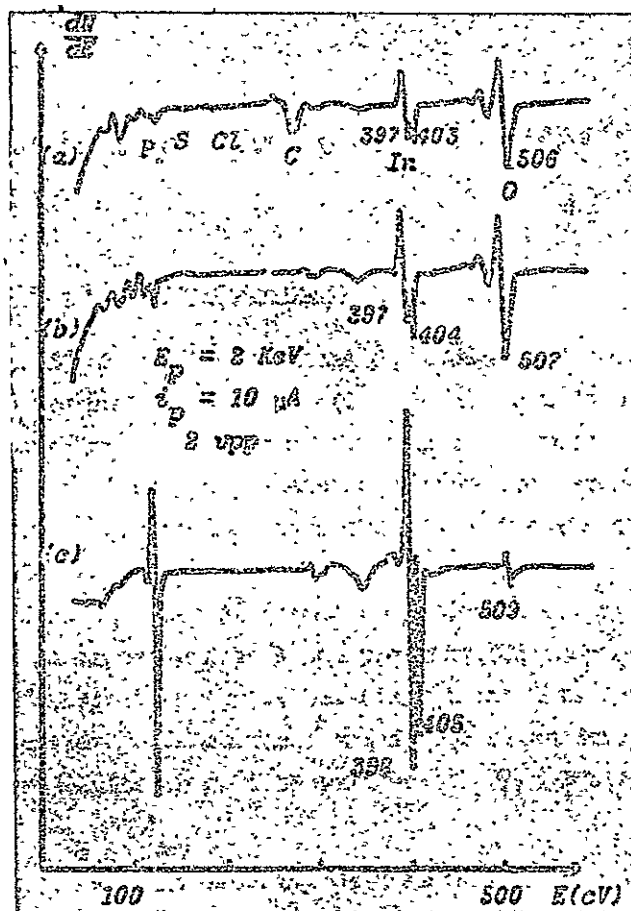
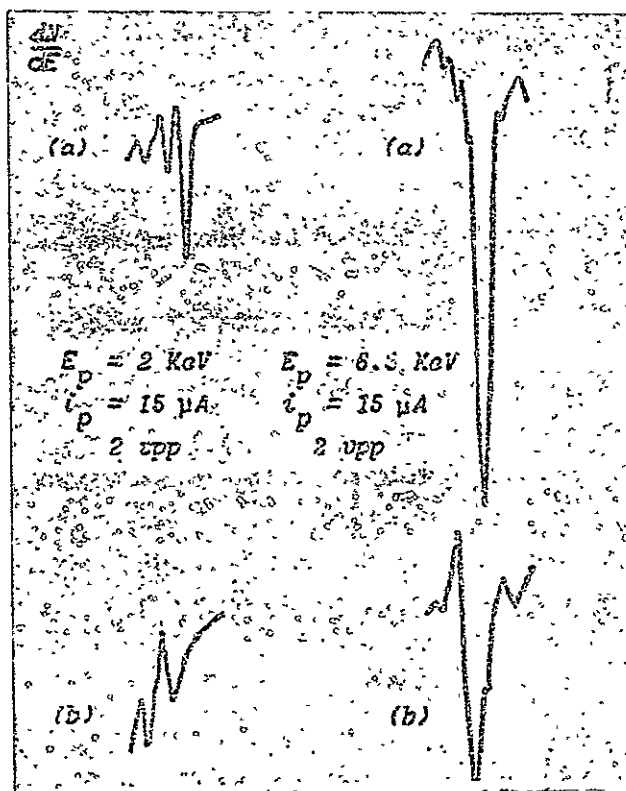Figure 3.   Evolution of Auger spectra under oxidation of InP.

Figure 4.   Evolution of low- and high-energy phosphorus peaks under oxidation of InP.

The most interesting result and the one which has received the most attention is that one concerning the loss observed near 20 eV, which has been attributed to a transition from the 3d Ga state to an empty surface state band, located near the conduction band, originating in the broken bonds in gallium atoms at the surface. In fact, it can be noted that this peak decreases very noticeably to the extent that the arsenic recovery of the surface increases, and almost disappears when the latter approaches 1. On the other hand, if one compares the energy of this transition ($\simeq$ 20 eV) to that of the 3d Ga level with respect to the height of the valence band (19 eV /8/), one can locate the surface state band, which is brought into play, within approximately 1 eV of the height of the valence band, i.e., in the forbidden band (Eg = 1.4 eV). Nevertheless, it should be noted that this peak, near 20 eV, is also observed for the (110) cleavage plane [5,9], although in this case it now appears to be well established, by various techniques such as photoemission [10] or the Kelvin probe [11], that there are no surface states in the forbidden band. In order to explain this apparent contradiction, several authors have proposed, for this type of transition, a strong excitonic coupling [12]. The energy of the exciton associated with this transition would be near 0.5 eV, thus forcing the location of the empty surface states out of the forbidden band.

In the same manner, the great sensitivity of this transition to the adsorption of oxygen (which also confirms the nature of its surface), as shown in Figure 6, which can be seen as proof of the preferential creation of Ga-O bonds [5], can also be attributed to the modification of the dielectric properties of the surface which entail the extinction of the excitonic transition [13]. (Nevertheless, in favor of the former hypothesis, it should be noted that we have observed a distinct increase in the oxygen adhesion coefficient of a stabilized gallium surface, over that of a stabilized arsenic surface [4].)

If one now considers the peaks observed at approximately 10 and 8.5 eV and which are not found again, either in the volume loss func-
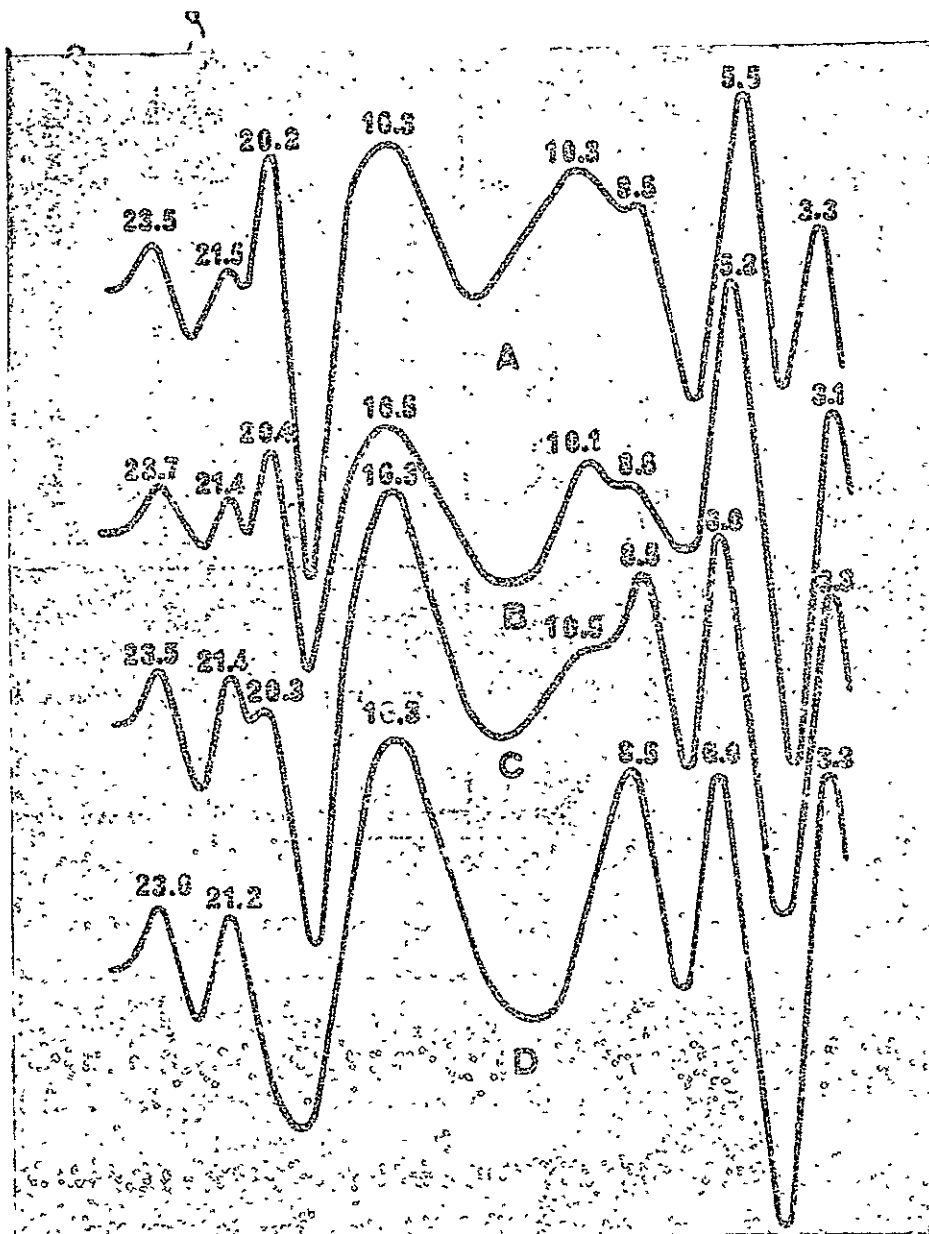
Figure 5. Low-energy electron spectra for GaAs (001).

KEY:

A : (4x1) on (1x6)		O	Θ_{As}	0.5
B : c(2x8)			Θ_{As}	0.5
C : c(4x4)		0.5	Θ_{As}	1
D : (1x1)			Θ_{As}	1

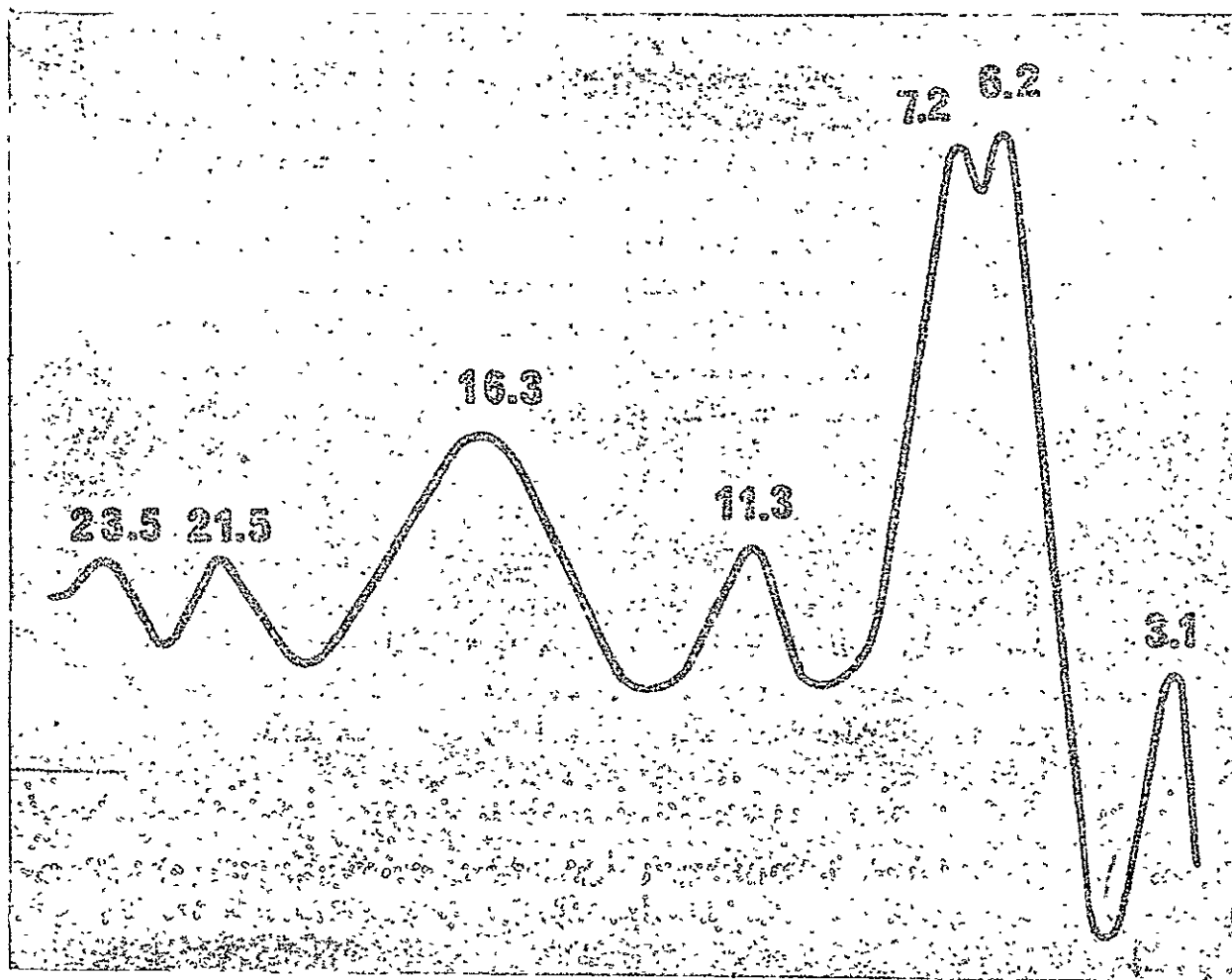Energy of primary electrons: 70 to 100 eV
Resolution: 0.2 eV

Figure 6.   Low-energy electron spectra for GaAs (001) in
interaction with oxygen.

3.3 Electronic Surface Properties

Given the fact that the GaAs and InP surfaces can be more or less rich in one of the III or V elements, one can therefore reconstitute surfaces containing more or fewer broken III or V bonds. Certain surface states related to these broken bonds are identified and, to a certain extent, located on the energy spectrum by means of low-energy electron spectroscopy (SPEEL). This technique consists of determining the energy losses of electrons bombarding a given surface. For example, these losses are due to plasmons (of volume or of surface), to inter-band transitions, etc. The inter-band transitions can affect surface states, in which case said transitions should vary with the density of surface states.

The SPEEL spectra are presented in the following form: $d^2N(E)/dE^2 = f(E_o - E)$, with E_o representing the energy of the primary beam.

3.3.1 GaAs (001)

Figure 5 illustrates the spectra of a series of samples with, successively, superstructures ranging from (4x4) to (1x1), i.e., with an increasing rate of arsenic recovery θ_{As}. These spectra generally agree well with the "energy loss" functions $-Im\ \varepsilon^{-1}$ (volume function) and $-Im\ (\varepsilon + 1)^{-1}$ (surface loss function) deduced from conventional optical data (see Table 2).

In these spectra, a certain number of peaks do not develop with θ_{As} (peaks at 3.3, 6, 16.5, 21.5 and 23.5 eV), and others decrease in amplitude when θ_{As} increases. There are peaks at 10.3 and 20 eV. Before attempting to explain these peaks, it should be noted than when this study began, an analogous study had been done by IBM. Their results, published in 1975 [5], agreed well with ours with respect to surfaces corresponding to the A, B and D spectra. The C spectrum corresponding to the c(4x4) superstructure is new, and one will note that it fits well, as expected, between the two B and D spectra for surfaces whose arsenic recovery rates θ_{As} are lower and higher, respectively. /14

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TABLE 2

ENERGY LOSSES (eV) OBSERVED FOR GaAs (001)

"4x6"	c(2x8)	c(4x4)As	(1x1)	A	Attribution
3.3	3.1	3.3	3.3	3.4	transitions interbandes (volume) B
5.5	5.8	6.0	6.0	8.0	
8.5	8.6	8.5	8.5	(8.8)	transitions interbandes (surface?)
10.3	10.1	10.5			C
16.3	16.5	16.3	16.3	15.9	
20.2	20.4	20.3			transition 3d(Ga) Etat de surface (Ga) D
21.5	21.4	21.4	21.2	21.5	D^1 (transitions 3d(Ga) → BC)
23.5	23.7	23.5	23.6	23.2	D^2 (transitions 3d(Ga) → BC)

KEY: A. Energy loss functions (deduced from data of H.R. Philipp
and H. Ehrenreich, Phys.Rev. 129, 1550 (1963)

B. Inter-band transitions (volume)

C. Inter-band transitions (surface?)

D. Surface state (Ga)

tion or in the results of high-energy electron spectroscopy, it is tempting to consider them as causing surface processes. In fact, a peak at 8.5 eV is adequately accounted for by the surface loss function, as corresponding to a surface plasmon $(\hbar\omega_s)$, but this value does not agree with the experimental value of 11 eV which we observed through SPEEL for grazing incidence (primary beam at 200 eV) [4]. Therefore, it seems probable that these two peaks are caused by surface states due to bonds directed towards the interior of the crystal, and whose hybridization differs from that of the bulk material ("back-bonds").

The essential conclusion to be drawn from study of the electronic properties of GaAs (001) is that, if one adequately determines the surface states, it is difficult to locate them precisely. A comparison of our results with those obtained and published very recently by other researchers utilizing other techniques [10,11] nevertheless allows one to suppose that the empty surface state band associated with broken gallium bonds is not located within the forbidden band.

3.3.2 InP (001)

The spectra of characteristic losses obtained for different InP (001) superstructures are summarized in Figure 7. If, as an energy reference, one takes the energy of the 4d level of the indium with respect to the height of the valence band (17 eV) published by Gudat and Eastman [14], the peak observed for InP (001) In (4x2) at 17.5 eV corresponds to an excitonic transition from the 4d level of the indium to the empty surface state band (see Table 3), analogous to that observed around 20 eV in the case of GaAs. The surface nature of this transition is confirmed by the decrease, if not the disappearance, of the peak by arsenic adsorption [InP (001) As (2x4)] or by phosphorus adsorption [InP (001) P (1x1)]. The evolution of the rest of the spectrum with the surface composition is less clear. The arsenic adsorption causes the peaks at 19.7, 11.5 and 8.5 eV to disappear, while a /19 new peak appears at 10.3 eV (see Figure 7b). The adsorption of the phosphorus, leading to the (1x1) [form], more simply tends to "amor-
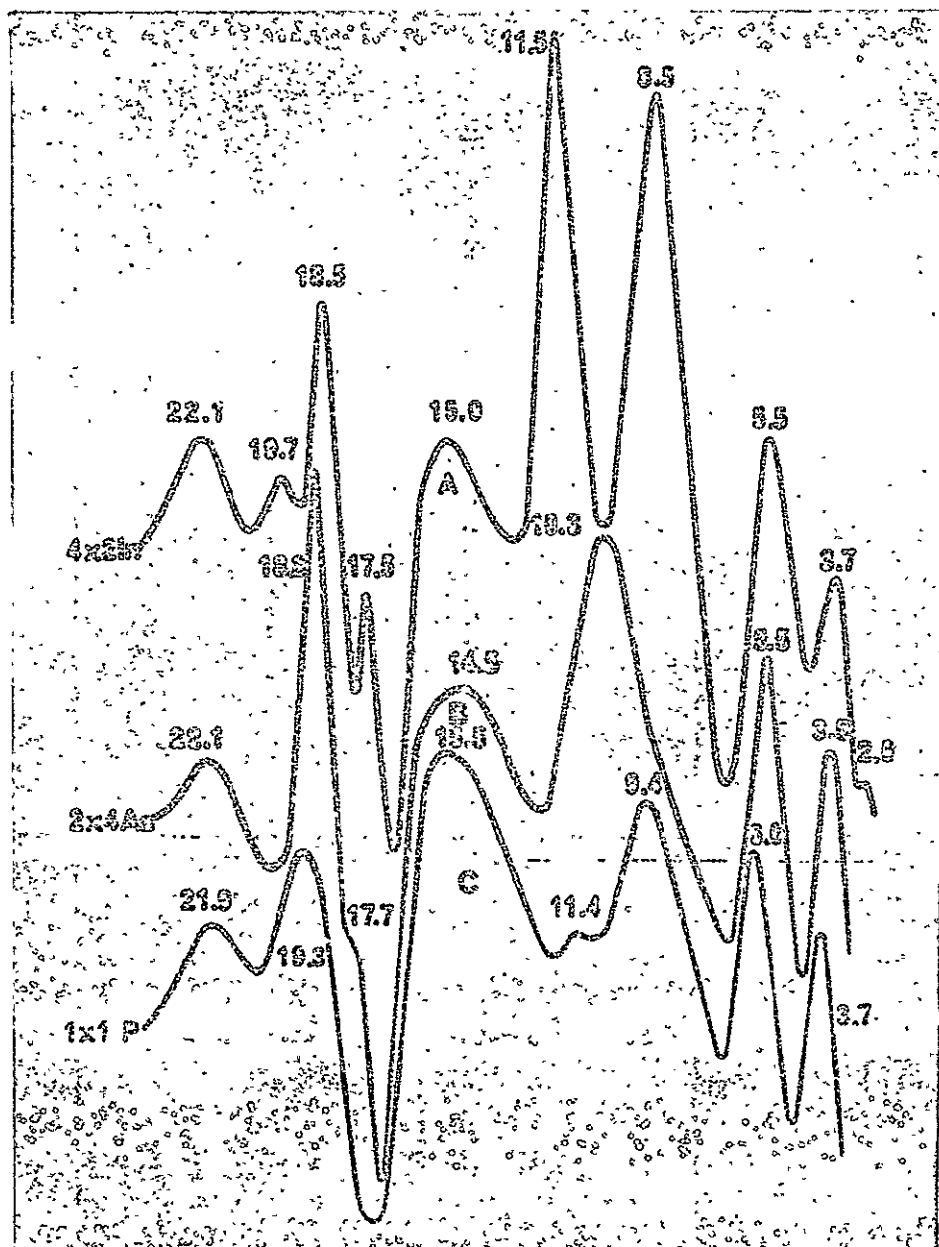
Figure 7. Low-energy electron spectra for InP (001)

A: InP (001) In (4x2)
B: InP (001) As (2x4)
C: InP (001) P (1x1)

TABLE 3

ENERGY LOSSES (eV) OBSERVED FOR InP (001)

4x2 In	2x1 As	1x1 P	Attribution
(2.6)			
3.7	(3.5)	3.7	transition interbandes
5.5	5.5	6.0	(volume) A
6.5			
		9.4	transitions interbandes
	10.3		(surface ?) B
11.5		11.4	
15.0	14.5	15.5	C
17.45	17.7		transition 4d(In) $\longrightarrow$ État de surface (In)
18.5	18.0		D^1_{In}
19.75		19.3	$D^1_{In} + \Delta d$
22.1	22.1	21.9	D^2_{In}

KEY: A. Inter-band transitions (volume)
      B. Inter-band transitions (surface?)
      C. Surface states (In)

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phize" the spectrum, as illustrated by a comparison of the spectrum
we obtained with the absorption spectrum shown in Figure 1 of refer-
ence [15].

With respect to the problem of the existence of surface states
within the gap which particularly concerns us, one meets again with
the difficulty previously encountered with GaAs, to wit: if energy-
loss spectroscopy demonstrates at least one surface transition for
In (001), the energy level of the final state (surface state) of this
transition is ambiguous, probably because of its excitonic nature.

3.4 Creation of a Schottky Contact by in situ Metallization

In spite of some uncertainty concerning the energy level of sur-
face states due to broken gallium bonds, or broken indium bonds, we
postulate (along with other research teams) that this level is loca-
ted just below the conduction band. In other words, there are no in-
trinsic surface states located within the gap. Then, what determines
the Schottky barrier? Is it determined by extrinsic surface states
caused by contaminants, or by the metal itself?

Careful in situ metallization experiments on clean and contamin-
ated surfaces were therefore carried out.

3.4.1 GaAs (001)

In the interest of clean operating methods, we selected the same
metallization technique which we utilized in "Application of an Epitax-
ial Layer by Molecular Sprays" [4], i.e., evaporation starting with a
Knudsen cell such as those described in DRME research report No. 74 34
296.

The metal we selected was silver, due to the value it appeared   /20
to provide in the case of metal/indium phosphide contact [16] which
motivated this study.

Metallizations were carried out on epitaxial layers or on type n
substrates with a concentration of free carriers on the order of

10^{16} at 3×10^{17} cm^{-3}. The vacuum in the chamber, which initially is on the order of 2×10^{-10} Torr, does not increase to more than 2 to 5×10^{-9} Torr during evaporation.

Several metallization series were carried out on surfaces with GaAs (001) As (1x1) and GaAs (001) Ga c(8x2) superstructures, and on a surface which had not been cleaned <u>in situ</u>, and which therefore was to a great extent contaminated by oxygen. After making diodes with diameters of 500 microns by photolithography, I-V measurements were made which enabled us to determine the value of the Schottky barrier. These values are summarized in Table 4.

TABLE 4

EFFECT OF THE NATURE OF THE GaAs (001) SURFACE
ON THE VALUE OF THE SCHOTTKY BARRIER

Nature de la surface A	Référence B	ϕ_{Bn} eV
oxydée C	P 10	0.80 ± 0.2
GaAs(001) Ga (8x2)	DMI 21	0.70 ± 0.2
	DMI 51	0.64 ± 0.2
GaAs(001) As (1x1)	DMI 32	0.60 ± 0.2
	DMI 52	0.62 ± 0.2
	P 8	0.60 ± 0.2

KEY: A. Nature of the surface
      B. Reference
      C. Oxidized

First of all, we observed that the Schottky barrier obtained on an oxidized surface has the value 0.80 eV, in accordance with values published in the literature. Such is not the case for results corre- /21 sponding to the other surfaces studied. In particular, the diodes created on surfaces rich in arsenic present a barrier which is clearly weaker (0.60 eV) than those which are usually observed. With re-

spect to diodes created on surfaces rich in gallium, the Φ_{Bn} barrier fluctuates from one experiment to another, between 0.60 and 0.70 eV. Moreover, we noted the following interesting properties:

Metallization on an oxidized surface yields a polycrystalline silver deposit. On the other hand, when metallization is carried out on the GaAs (001) Ga c(8x2) surface, which is rich in gallium, the deposit is monocrystalline and is in epitaxy with the GaAs. The LEED patterns indicate that the epitaxial relation takes place between the (001) plane of the GaAs and the (110) plane of the silver. If one considers the structural characteristics of the two substances (GaAs: zinc blende a = 5.65 angstroms and Ag: c.f.c. a = 4.08 angstroms), one notices that there exist two possibilities for epitaxy of Ag on GaAs, taking into account the relation $a_{GaAs}/a_{Ag} \sim \sqrt{2}$: the first is Ag (001)/GaAs (001) with the (100) axes rotated 45°, and the second is Ag (110)/GaAs (001) with coincidence of the Ag [100]//GaAs [110] axes. It is the latter epitaxial possibility which was realized. An analogous epitaxial relationship was also observed by Ludeke and Esaki [17] for the Al/GaAs pair. The silver deposits on the GaAs (001) As (1x1) plane rich in arsenic only shows an epitaxial relationship if the substrate is heated to 450°C. The exact arrangement of the silver atoms with respect to the GaAs atoms has not yet been clarified.

3.4.2 InP (001)

As a result of the work carried out on GaAs, study of the metal/InP contact is less advanced. First of all, we considered the phenomenon of the diffusion of chemical elements on an oxidized Au-InP diode, annealed at 340°C. The concentration profiles were obtained through measurement of the intensities of Auger signals recorded during ion milling. Figure 8 illustrates these profiles as a function of the duration of ionic bombardment. One notes that the indium diffuses enormously towards the metal and that oxygen is found there in great quantities. Utilizing the internal calibration technique developed by Hammer et al. [18] for quantitative analysis of pseudo-binary systems, we /23
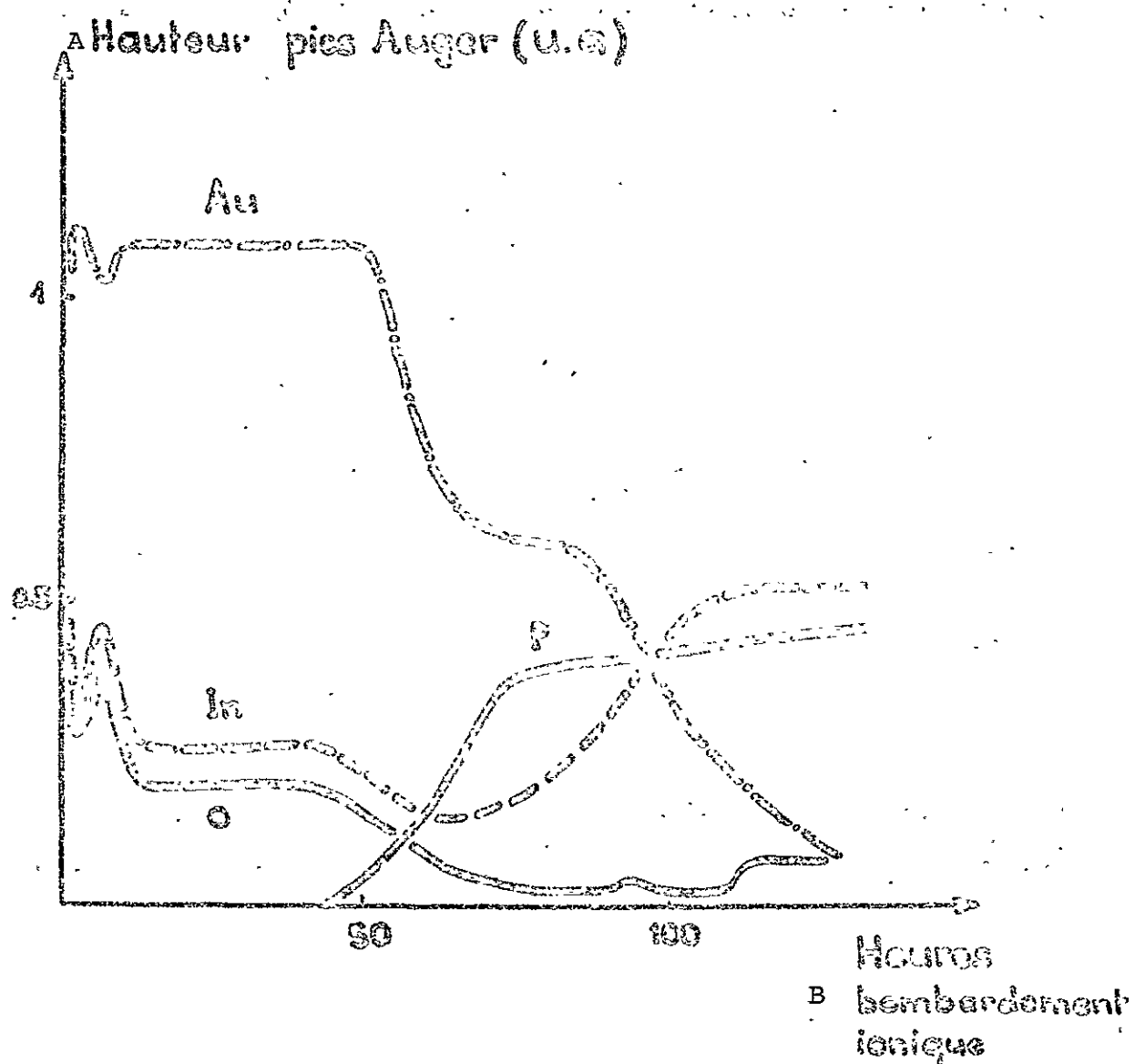
Figure 8. Auger profiles of an Au (5,000 Å)/InP Schottky
diode annealed at 340°C.

KEY: A. Height of Auger peaks
        B. Hours of ionic bombardment

were able to show that the simultaneous presence of indium and oxygen is due to the formation of In_2O_3.

Following the same procedure as for GaAs, we attempted to create silver deposits on surfaces with various compositions: InP (001) In (4x2), InP (001) P (1x1), InP (001) As (2x4), and an oxidized surface. The results which we currently possess concern essentially the (4x2) surface which is rich in indium.

Given that the mesh parameter of InP is 5.87 angstroms, and that that of silver is 4.08 angstroms, we again find $a_{InP}/a_{Ag} \sim \sqrt{2}$, as in the case of GaAs. Therefore, one might think that metallization on a surface rich in indium yields an epitaxy. For three metallizations we carried out, no epitaxy was observed. The Schottky barrier measured was 0.40 eV. The diode has a rather significant leakage current. The low quality of the diode and the Φ_{Bn} value obtained for this metallization are analogous to those which were previously published in the literature with respect to metallizations on oxidized InP surfaces [19].

Very recently, Farrow [20] reported a result for silver metallization on a phosphorus-rich InP (001) P c(2x8) surface: there was epitaxy, and the contact is ohmic.

3.4.3 Conclusion with Respect to the Variation in Φ_{Bn}

The results which we have obtained lead us to formulate the following hypotheses:

A. The value of the Schottky barrier Φ_{Bn} depends on the oxygen contamination of the metal/semiconductor interface. An oxidized surface (reference P8 in Table 4) shows a higher barrier than does a clean surface. The fluctuations in Φ_{Bn} which were observed on gallium-rich surfaces are therefore attributed to a partial contamination of these surfaces by oxygen. In fact, we have already shown (in the preceding DRME study [4]) that the gallium-rich surface is more oxidizable than is the surface rich in arsenic. This result is confirmed by a publication by Ludeke and Koma [5]. There-

fore, it is probable that the gallium-rich surface is parti-
ally contaminated by oxygen during evaporation of the metal.

B. The value of Φ_{Bn} is related to the structural state of the
interface. In the case of silver, intimate contact with InP
appears to lower the Φ_{Bn} barrier, since it is a question of
going from a Schottky contact with an 0.40 eV barrier for a
non-epitaxial deposit to an ohmic contact for an epitaxy.

Until new experimental proof is available, both of the two formu-
lated hypotheses can be retained, and it is probable that the two ef-
fects, chemical and structural, are produced conjointly.

4. Conclusions

This study of surface properties and its application to the real-
ization of Schottky contacts was conducted concurrently on GaAs and InP.

Utilization of the molecular spray technique made it possible to
obtain for both these semiconductors (001) surfaces with different com-
positions. These surfaces thus show superstructures which are identi-
fiable by low-energy electron diffraction, and are related to the super-
ficial composition.

Through low-energy electron spectroscopy, we have verified elec-
tronic surface states created by broken bonds ("dangling bonds"). Nev-
ertheless, the nature of transitions related to these states (excitonic
nature), as well as the limitations of the technique utilized (energy
reference mark), do not allow a precise determination of the energy
levels of these electronic surface states. With reference to results
recently published in the literature, we locate these energy levels
outside the forbidden band. Thus, these states cannot be responsible
for determination of the Schottky barrier according to the Bardeen mod-
el.

In situ metallizations of silver on surfaces with different com-
positions yield diodes whose Schottky barrier values Φ_{Bn} appear to de-
pend on said compositions. On the other hand, the metallic deposit

is in epitaxy with the semiconductor. The variation in Φ_{Bn} can thus be attributed to a chemical effect of the interface (composition, contamination, etc.) and/or a structural effect bringing into play the metal/semiconductor bonds. More thorough and more systematic research, for example, by measurement of the work function at surfaces which are or are not covered by contaminants and metal, should make it possible to resolve this indeterminacy.
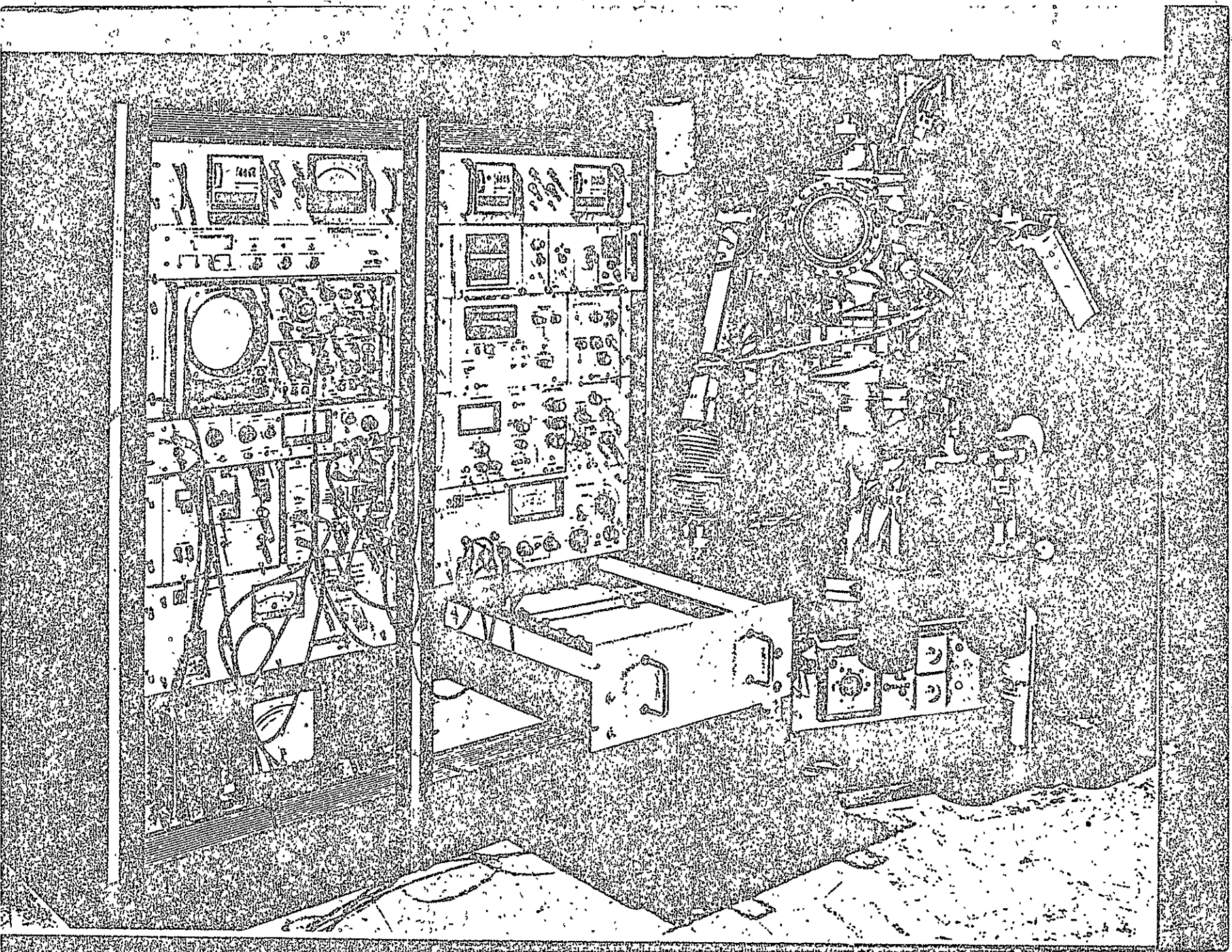
From the point of view of potential applications of the results of this study, we emphasize especially the achievement of Schottky contacts with weak barriers on GaAs (0.6 eV). Such contacts are noteworthy in the manufacture of microwave components (mixer diodes).

Acknowledgements

<div align="center">REFERENCES</div>

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